Characterization of Mineral Matter in Sub-bituminous Coals by AIA-SEM

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ABSTRACT

Automated image analysis (AIA) was used with scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy to characterize the mineral matter in two western sub-bituminous coals from the Adaville No. 11 seam (Kemmerer, WY) and the Dietz No. 1 & 2 seams (Decker, MT). The samples were ground to -200 mesh and cleaned by float-sink separation at 1.40 and 1.38 sp. gr., respectively. The particles were characterized before and after cleaning for mineral phase and size distributions by classifying them into 6 sizes and 16 mineral categories. Quartz was the dominant mineral in both coals, with the Adaville sample containing primarily quartz and an iron-rich mineral. Traces of apatite were also detected in the Adaville samples. The Dietz coal contained primarily quartz and kaolinite. Preliminary results are also presented for the association of the mineral particles with the coal matrix. These analyses were performed by automatically classifying the composite mineral-coal features into 10 types of particles of increasing specific gravity. The results closely estimated the total mineral matter content, as calculated from the ASTM ash content, and the specific gravity distributions were consistent with data obtained from the cleaning step.

INTRODUCTION

Scanning electron microscopy (SEM) in conjunction with energy-dispersive x-ray spectroscopy can provide in-situ characterization of mineral particles in coal for size, shape, chemical identity, and relation to the coal matrix. Automated image analysis (AIA) techniques are currently available to permit rapid SEM characterization of statistically significant numbers of particles, providing data for the size distribution of individual minerals as well as for the the total mineral matter content. These data can aid in the decision-making process about the extent of grinding needed for effective liberation of mineral matter from coal. AIA-SEM has a decided advantage over other techniques, such as the ASTM ash determinations which provide no information on the original mineral or size distributions, or x-ray diffraction or FTIR analyses which require time-consuming sample preparation but cannot provide size information. Since the AIA data permit cleaning effectiveness to be evaluated with respect to both mineral phase and particle size, problems with the removal of certain particle sizes or phases can be detected and remedied.

AIA-SEM has been used previously at the Ames Laboratory for the characterization of several series of physically and chemically processed bituminous coals (1-3). In this study, AIA-SEM was applied to two sub-bituminous coals before and after physical cleaning. In addition, preliminary results are presented for the direct measurement of the extent of association of mineral particles with coal.

EXPERIMENTAL

Coal Sample Description

Two coals, from the Adaville No. 11 seam (Kemmerer, WY) and from the Dietz No. 1 & 2 seams (Decker, MT), were ground to nominal 200 mesh (~70-80% less than 74 μm), typical of coals introduced into pulverized fuel boilers, and were cleaned in a halogenated hydrocarbon to produce a superclean product with a target ash level of ~3%, using specific gravities of 1.40 and 1.38, respectively. The raw and clean coal fractions were analyzed by standard ASTM techniques for moisture, ash, and sulfur levels (see Table 1). Because both raw coals had low levels of sulfur and moderate levels of ash, typical of western coals, only ~56% of the mineral matter was removed from the Adaville coal, and only ~30% of the mineral matter was removed from the Dietz coal.

Table 1. Analyses of Raw and Cleaned Coals[a]

	Adaville No. 11		Dietz No. 1 & 2	
	Raw	Clean	Raw	Clean
Rank	subB		subA	
Moisture	22.15	11.29	19.82	11.96
Pyritic S	0.03	0.01	0.02	0.02
Sulfate S	0.03	0.01	0.02	0.01
Organic S	0.81	0.70	0.51	0.36
Total S	0.86	0.71	0.56	0.40
Ash	9.20	4.07	5.31	3.70
Mineral Matter[b]	10.41	4.60	6.01	4.19
% MM Removed	---	55.81	----	30.28

[a] Values are expressed as wt. % on a dry basis, except for moisture which is presented on an as-received basis.
[b] Calculated by modified Parr formula, as defined in ref. 4: Mineral matter = 1.13(ash) + 0.47(pyritic sulfur)

Procedures

Since details of the AIA-SEM mineral analyses were described elsewhere (1,2), only the mineral-coal association analysis procedure will be described in this paper. One set of coal-epoxy pellets was prepared using standard petrographic techniques for the AIA mineral study. A second set of pellets was prepared for the association study of the mineral particles with the coal. For these pellets, 2 g. of coal were mixed with 8 g. of melted Carnauba wax, placed in a 1-in. diameter mold under pressure, and allowed to cool. The solid pellets were ground to expose a cross section, polished, and coated with ~50 Å of carbon to provide a conductive surface for SEM examination.

Analysis Hardware. In addition to the AIA-SEM system previously described (1,2) for mineral analyses, a LeMont Scientific OASYS image analyzer system was employed for the mineral-coal association studies. The OASYS image analyzer can process entire images at a time, whether they be from an SEM or a TV camera, and can analyze up to 16 different gray-levels of particles with capabilities for image enhancement and processing.

SEM Conditions. For both types of studies, samples were analyzed in the SEM with an accelerating potential of 25 kV and a beam current of ~4 nA, using the backscattered electron signal since it is especially sensitive to the average atomic number of a phase in a polished cross section. Therefore, mineral particles stand out much brighter than coal particles.

AIA-SEM Association Analyses. The LeMont OASYS image analyzer was used for the preliminary automated association studies. A minimum of 24 fields were digitized for each sample over a range of magnifications from 50x to 300x and recorded on magnetic disk. Thousands of coal and mineral particles were represented by these images.

The intensity of the backscattered electron signal was divided into four segments of increasing brightness to encompass signals from the mounting medium, the coal particles, most minerals, and finally pyrite. The OASYS "Linescan" software package was used to measure the area of associated coal, pyrite, and other mineral particles for each composite feature while keeping track of the association of the individual features. A pixel density of 512 points across the screen was fixed by the OASYS hardware.

Composite coal-mineral features were assigned by the relative abundance of the phases, determined according to gray level, into one of six specific gravity classes (<1.3, 1.3-1.4, 1.4-1.5, 1.5-1.6, 1.6-1.7, and 1.7-1.8) or into four special classes (pure coal, pure pyrite, pure "other" minerals, or a pyrite/mineral mixture). Composites were also classified into the same six size ranges used for the mineral analyses.

RESULTS AND DISCUSSION

Mineral Analyses

The AIA results for the raw and cleaned Adaville and Dietz coals presented in Tables 2a-c and 3a-c, respectively, provide much more insight into the nature of the mineral matter in these samples than do the ASTM results. The data presented are for minerals in the raw coal, minerals in the clean coal, and the percent removal of mineral matter in each size-mineral class. In all cases, the data are presented as weight percent of dry coal.

In Table 2a, results for the raw Adaville coal indicate that the primary mineral phases are quartz and an iron-rich phase. No conclusive identification is presently available for the iron-rich phase, but iron hydroxides are likely candidates. These mineral matter characteristics are in contrast to previous findings for midwestern bituminous coals (1,2), in which the predominant minerals were pyrite, quartz, kaolinite and illite. The particle size distribution of the minerals was notably coarse; about 44% of the mineral matter was larger than 36 μm.

The AIA results also showed the presence of apatite. The amount found was small (0.62% of the dry coal), but it was confirmed by the presence of very small peaks at the appropriate locations in x-ray diffraction patterns. Although this mineral is not unusual for western coals and it does not pose any particular environmental hazard, its detection at such low levels is interesting and demonstrates the utility of the AIA-SEM technique for detecting small amounts of discrete phases as they occur disseminated throughout a matrix. The other minerals in the raw coal were present in smaller amounts and consisted of kaolinite, illite, montmorillonite, pyrite, and other miscellaneous phases.

Table 2a. AIA Results for Raw Adaville Coal (200 mesh x 0), Expressed as Weight Percent of Dry Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	0.04	0.00	0.01	0.01	0.01	0.05	0.12
KAOLINITE	0.04	0.11	0.06	0.11	0.09	0.13	0.53
ILLITE	0.00	0.04	0.03	0.02	0.02	0.21	0.32
MONTMORILLONITE	0.00	0.00	0.02	0.02	0.04	0.18	0.26
QUARTZ	0.32	0.42	0.20	0.35	0.47	1.68	3.44
APATITE	0.04	0.04	0.06	0.07	0.07	0.35	0.62
FE-RICH	0.07	0.14	0.09	0.15	0.16	1.57	2.18
SILICATES	0.00	0.00	0.02	0.04	0.03	0.11	0.20
OTHER	0.46	1.30	0.29	0.33	0.14	0.25	2.76
TOTALS	0.95	2.03	0.77	1.10	1.03	4.53	10.41

Table 2b. AIA Results for Clean Adaville Coal (Floated at 1.4 Sp. Gr.), Expressed as Weight Percent of Dry Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	0.02	0.02	0.01	0.02	0.01	0.00	0.08
KAOLINITE	0.08	0.11	0.04	0.02	0.02	0.00	0.27
ILLITE	0.02	0.02	0.01	0.01	0.00	0.00	0.05
MONTMORILLONITE	0.01	0.00	0.00	0.00	0.00	0.00	0.01
QUARTZ	0.68	0.94	0.34	0.48	0.37	0.09	2.90
APATITE	0.05	0.14	0.02	0.01	0.00	0.00	0.22
FE-RICH	0.10	0.12	0.04	0.03	0.01	0.00	0.31
SILICATES	0.03	0.04	0.01	0.01	0.01	0.00	0.10
OTHER	0.12	0.30	0.07	0.07	0.06	0.04	0.66
TOTALS	1.10	1.69	0.54	0.66	0.48	0.13	4.60

Table 2c. Percent Removal of Mineral Matter from Adaville Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	31	--	45	-242	14	100	33
KAOLINITE	-115	-9	33	78	80	100	48
ILLITE	--	57	62	51	100	100	83
MONTMORILLONITE	--	--	92	93	100	100	95
QUARTZ	-114	-124	-73	-37	23	95	16
APATITE	-29	-295	58	91	100	100	66
FE-RICH	-46	12	54	80	93	100	86
SILICATES	--	--	48	70	60	100	49
OTHER	73	77	77	79	55	84	76
TOTALS	-16	17	30	40	54	97	56

Table 3a. AIA Results for Raw Dietz Coal (200 mesh x 0), Expressed as Weight Percent of Dry Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	0.07	0.05	0.10	0.00	0.07	0.07	0.35
KAOLINITE	0.16	0.23	0.28	0.50	0.20	0.00	1.38
ILLITE	0.02	0.01	0.06	0.02	0.15	0.00	0.26
QUARTZ	0.21	0.24	0.22	0.43	0.59	0.36	2.05
CALCITE	0.11	0.09	0.08	0.03	0.00	0.00	0.31
SILICATES	0.04	0.06	0.05	0.01	0.06	0.00	0.22
OTHER	0.46	0.42	0.29	0.20	0.07	0.00	1.44
TOTALS	1.07	1.12	1.07	1.19	1.13	0.43	6.01

Table 3b. AIA Results for Clean Dietz Coal (Floated at 1.38 Sp. Gr.), Expressed as Weight Percent of Dry Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	0.04	0.05	0.06	0.10	0.00	0.00	0.25
KAOLINITE	0.06	0.14	0.18	0.23	0.22	0.12	0.95
ILLITE	0.00	0.01	0.02	0.03	0.00	0.00	0.06
QUARTZ	0.27	0.30	0.29	0.28	0.11	0.00	1.24
CALCITE	0.03	0.03	0.03	0.03	0.02	0.00	0.14
SILICATES	0.09	0.05	0.04	0.01	0.00	0.00	0.19
OTHER	0.41	0.46	0.14	0.11	0.17	0.06	1.36
TOTALS	0.90	1.04	0.76	0.80	0.52	0.18	4.19

Table 3c. Percent Removal of Mineral Matter from Dietz Coal

Mineral Phase	Size, μm <4	<7	<12	<21	<36	>36	TOTALS
PYRITE	35	2	30	--	100	100	74
KAOLINITE	60	31	29	48	-23	--	22
ILLITE	75	-15	64	-47	100	--	73
QUARTZ	-44	-39	-49	28	80	100	32
CALCITE	72	66	52	-6	--	--	51
SILICATES	-178	15	12	-14	100	--	4
OTHER	1	-22	46	34	-186	--	-5
TOTALS	6	-4	20	25	49	83	30

For the Adaville coal (Tables 2a-c), little of the mineral matter finer than 36 μm was removed. In the raw coal, 44% of the mineral matter was larger than 36 μm in diameter. From ASTM data (Table 1), only 56% of the mineral matter was removed. Data in Tables 2a-c show that removal of mineral matter from the >36 μm size class accounted for 76% of all the mineral matter removed; the removal was progressively less for the smaller size classes.

The Dietz coal shows similar trends (Tables 3a-c). The mineral matter in the raw coal was dominated by quartz, followed by kaolinite, and then other minerals. However for this coal, the mineral matter was spread over the entire particle size range. Only 26% of the mineral matter was in the two largest size classes (i.e., >21 μm). Of the 30% of the mineral matter was removed during cleaning, 47% was due to the removal of particles larger than 21 μm. Much smaller reductions in mineral matter are noted for the finer size ranges.

It would appear that for both raw coals, the mineral particles were disseminated widely throughout the coal and were intimately associated with the organic matter, so that even at a nominal size of 200 mesh, relatively little mineral matter could be removed by float-sink cleaning. Use of AIA to measure directly the extent of mineral-coal association should help to confirm this.

Association Studies

Preliminary results from the association studies of minerals and coal are given in Table 4. The data are weight fractions of dry coal measured for each particle type. In Table 5, data are presented for comparing ASTM and direct AIA measurements of pyrite and mineral matter content. AIA mineral content was obtained by calculating a weighted area fraction of pyrite and mineral particles as compared to all particles in the cross section. The pyrite estimates of the AIA mineral study were taken from Tables 2a-3b, which were normalized to the mineral matter content calculated from ASTM ash values. The data show reasonable agreement among the measurements, given the preliminary nature of this study, lending credence to the validity of the association results in Table 4. Further work is in progress to improve the agreement.

Summing the weight fractions of the classes of the raw coals (in Table 4) that are lighter than 1.4 sp. gr. should predict the yield for the separation process, that is, 80.41% for the Adaville and 95.28% for the Dietz coal. Actual recovery data are not available for these samples so that direct comparison is not possible. Such data will be secured for future tests. Summing the fractions heavier than 1.4 specific gravity for the clean coals should estimate the amount of minerals misplaced during cleaning. Since less than 1% of the Adaville and less than 2% of the Dietz coals fall in this category, these values appear quite consistent with a float-sink separation for a nominal 200 mesh particle size.

The direct association program appears to have correctly classified the composite mineral particles into specific gravity classes for the Adaville coal. Significant material was found for most particle types in the raw coal, but it was concentrated in the lighter classes for the clean coal.

The results for the Dietz coal were quite different. Virtually the same amount of material was analyzed as being lighter than 1.4 sp.gr. for both the raw and clean coals (95.28% and 98.67%, respectively). In the raw coal, ~2.2% of the dry coal was analyzed as "Mineral matter-rich" (2.08%) plus "(Mineral + Pyrite)-rich" (0.12%). That material alone could account for the reduction of mineral matter from 6.01% to 4.19%, as shown in Table 1. It appears that this level

Table 4. Preliminary Analysis of the Association of Mineral Particles with Coal (Weight Percent of Dry Coal in Each Particle Type Class as Assigned by Gray Level)

Particle Type		Adaville 11 raw	Adaville 11 clean		Dietz 1 & 2 raw	Dietz 1 & 2 clean	
Pure coal	80.41	35.06	41.42	95.28	76.49	69.70	98.67
<1.3 sp.gr.		31.49	53.00		13.20	25.48	
1.3-1.4 sp.gr.		13.86	4.99		5.59	3.49	
1.4-1.5 sp.gr.		7.54	0.23	0.59	1.60	0.48	1.31
1.5-1.6 sp.gr.		6.47	0.06		0.37	0.19	
1.6-1.7 sp.gr.		0.96	0.05		0.18	0.05	
1.7-1.8 sp.gr.		1.44	0.03		0.35	0.03	
Mineral matter-rich		2.98	0.19		2.08	0.55	
Pyrite-rich		0.00	0.00		0.00	0.00	
(Mineral + Pyrite)-rich		0.17	0.03		0.12	0.01	
		99.97	100.00		99.98	99.98	

Table 5. Comparison of Direct AIA Measurements of Mineral Matter and Pyrite Content with ASTM Values

	Adaville 11 raw	Adaville 11 clean	Dietz 1 & 2 raw	Dietz 1 & 2 clean
Mineral Matter				
AIA[a]	11.37	2.97	4.00	2.43
ASTM[b]	10.41	4.60	6.01	4.19
Pyrite				
AIA[a]	0.19	0.03	0.13	0.04
AIA[c]	0.12	0.08	0.35	0.25
ASTM[d]	0.06	0.02	0.04	0.04

[a] from OASYS association analyses
[b] from Table 1, as calculated by modified Parr formula
[c] from AIA mineral analyses (Tables 2a-3b)
[d] calculated from ASTM pyritic sulfur content in Table 1

of mineral matter reduction could also have been achieved if the separation had been conducted at a higher specific gravity.

The distribution of mass over the entire range of densities is noteworthy for the two raw coals. A strong bimodal distribution indicates good liberation. In this sense, the mineral particles in the Dietz coal appear to be more liberated than those of the Adaville coal (76.49% vs. 35.06% pure coal particles, respectively, in Table 4). Also, there is no significant "middlings" material for the raw Dietz coal (i.e., in the 1.4-1.6 density range). It would appear that even though more mineral matter was removed from the Adaville coal, it must have been at a cost of lower recovery.

CONCLUSIONS

AIA-SEM was used to obtain a direct insight into the character of mineral matter with respect to both mineral phase and particle size distribution for two western coals. Significant differences were seen in the mineral phases in the raw Adaville and Dietz coals; also, major differences were observed in the size distributions. For example, minerals in the Adaville sample appeared to be much coarser. This technique permitted characterization of low levels of mineral matter that resulted from deep cleaning and documented the selective removal of mineral matter of certain sizes. Correlation of the mass fraction of larger mineral particles and the amount of mineral matter removed suggests that only the larger mineral particles were liberated.

The AIA-SEM technique was used to measure directly the extent of coal mineral association and to produce a particle type distribution curve, relatable to specific gravity, for both raw and clean coals. The direct measure of mineral matter and pyrite content agreed reasonably well with ASTM results. These results indicate that minerals in the raw Dietz coal were more liberated from the coal matrix than those in the Adaville coal.

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